XIV. *Continuation of the Experiments and Obſervations on the Specific Gravities and Attractive Powers of various Saline Subſtances.* *By* Richard Kirwan, *Eſq. F. R. S.*

Read April 11, 1782.

BEFORE I enter into a detail of the new experiments I have made in the proſecution of this ſubject, I muſt beg leave to rectify ſome miſtakes I have fallen into in my laſt paper.

1. In computing the quantity of acid taken up by 10,5 gr. of mild vegetable fixed alkali, I made no allowance for the ſmall quantity of earth it contains, *viz.* 0,7035 of a grain; but in large quantities of alkali, this proportion is conſiderable, and occaſioned a ſmall but ſenſible error in my ſubſequent calculations of the proportion of ingredients in neutral ſalts, the quantity of alkali being, by that fraction, leſs than I ſuppoſed it in 10,5 gr. This correction being made, it will be found, that 100 gr. of perfectly dry vegetable fixed alkali (abſtracted from the quantity of earth) generally contain 22,457 gr. of fixed air inſtead of 21, as I before determined; yet the former determination is right, where the earth is not ſeparated, yet may well be ſuppoſed to exiſt, as in the alkali of pearl-aſh, purified by three repeated calcinations and ſolutions. Hence alſo 100 gr. of ſuch alkali, free from earth, water, and fixed air, take up 46,77 gr. of the mineral acids, that is, of the mere

acid part; and 100 gr. of common mild vegetable alkali take up about 36,23 of real acid.

100 gr. of perfectly dry tartar vitriolate contain 30,21 of real acid, 64,61 of fixed alkali, and 5,18 of water. Cryſtallized tartar vitriolate loſes only 1 *per cent.* of water in a heat in which its acid alſo is not ſeparated in any degree, and therefore contains 6,18 of water.

100 gr. of nitre, perfectly dried, contain 30,86 of acid, 66 of alkali, and 3,14 of water; but in cryſtallized nitre the proportion of water is ſomewhat greater; for 100 gr. of theſe cryſtals, being expoſed to a heat of 180° for two hours, loſt 3 gr. of their weight, without exhaling any acid ſmell; but when expoſed to a heat of 200°, the ſmell of the nitrous acid is diſtinctly perceived. Hence 100 gr. of cryſtallized nitre contain 29,89 of mere acid, 63,97 of alkali, and 6,14 of water.

100 gr. of digeſtive ſalt perfectly dry contain 29,68 of marine acid, 63,47 of alkali, and 6,85 of water. 100 gr. of cryſtallized digeſtive ſalt loſe but 1 gr. of their weight before the ſmell of the marine acid is perceived; and hence they contain 7,85 gr. of water.

But the miſtake which coſt me moſt time and pains to correct was that which I fell into when I imagined, that the mixtures of oil of vitriol and water, and ſpirit of nitre and water, had attained their maximum of denſity when they had cooled to the temperature of the atmoſphere, which at the time I made my experiments ſtood between 50 and 60° of FAHRENHEIT. The former I had even ſuffered to ſtand ſix hours, which was much longer than was neceſſary for its cooling; but when the acid was ſo much diluted as to cauſe little or no heat, I allowed it to ſtand but for a very little time before I examined its denſity: yet ſeveral months after I found many of theſe

mixtures

mixtures much denſer than when I firſt examined them, and that at leaſt twelve hours reſt was requiſite before concentrated oil of vitriol, to which even twice its weight of water is added, attains its utmoſt denſity, and ſtill more when a leſſer proportion of water is uſed: thus, when I made the mixture of 2519,75 gr. of oil of vitriol, whoſe ſpecific gravity was 1,819, with 180 of water, I found its denſity ſix hours after 1,771; but after twenty-four hours it was 1,798: and hence, according to the reaſoning in the former paper, the accrued denſity was at leaſt ,064 inſtead of ,045 as I had formerly found it. But by uſing oil of vitriol ſtill more concentrated, whoſe ſpecific gravity was 1,8846, I was enabled, by a ſimilar train of reaſoning, to make a ſtill nearer approximation, and found that the accrued denſity of oil of vitriol, whoſe ſpecific gravity is 1,819, amounts to 0,104; and conſequently its mathematical ſpecific gravity is 1,715. 6,5 gr. of this oil of vitriol contained, as I before found, 3,55 of mere acid, and the remainder water, then the weight of an equal bulk of water is 3,79 gr.; and ſubtracting from this the weight of the water that enters into the compoſition of the oil of vitriol, it will be found, that the weight of a bulk of water, equal to the acid part, is 0,84, and conſequently the ſpecific gravity of the pure and mere acid part is 4,226. Upon this ground, and conſtantly allowing the mixtures to reſt at leaſt twelve hours (until the oil of vitriol was diluted with four times its weight of water, and then often only ſix hours) before their denſity was examined, I conſtructed the table hereto annexed; the temperature of the room I conſtantly kept between 50 and 60°.

Oil of vitriol.	Acid.	Water.	Accrued density.	Mathemat. sp. gravity.	
Grains.					
1000	- -	387,95	,07	1,877	1,846
1100	- -	487,95	,104	1,738	1,844
1200	- -	587,95	,105	1,637	1,742
1300	- -	687,95	,144	1,561	1,705
1400	- -	787,95	,144	1,500	1,644
1500	- -	887,95	,137	1,452	1,589
1600	- -	987,95	,137	1,412	1,539
1700	- -	1087,95	,130	1,379	1,509
1800	- -	1187,95	,124	1,350	1,474
1900	- -	1287,95	,116	1,326	1,442
2000	- -	1387,95	,116	1,304	1,420
2100	- -	1487,95	,112	1,286	1,398
2200	- -	1587,95	,112	1,269	1,381
2300	- -	1687,95	,108	1,254	1,362
2400	- -	1787,95	,104	1,241	1,345
2500	- -	1887,95	,104	1,229	1,333
2600	- -	1987,95	,101	1,219	1,320
2700	- -	2087,95	,096	1,209	1,307
2800	- -	2187,95	,091	1,200	1,291
2900	- -	2287,95	,090	1,192	1,282
3000	- -	2387,95	,090	1,184	1,274
3100	612,05	2487,95	,090	1,177	1,267
3200	- -	2587,95	,090	1,170	1,260
3300	- -	2687,95	,089	1,164	1,253
3400	- -	2787,95	,084	1,159	1,243
3500	- -	2887,95	,083	1,150	1,233
3600	- -	2987,95	,073	1,149	1,222
3700	- -	3087,95	,073	1,144	1,217
3800	- -	3187,95	,071	1,140	1,211
3900	- -	3287,95	,071	1,136	1,208
4000	- -	3387,95	,071	1,132	1,204
4100	- -	3487,95	,070	2,128	1,198
4200	- -	3587,95	,070	1,125	1,195
4300	- -	3687,95	,070	1,121	1,191
4400	- -	3787,95	,070	1,118	1,188
4500	- -	3887,95	,070	1,115	1,185
4600	- -	3987,95	,070	1,113	1,183
4700	- -	4087,95	,070	1,110	1,180
4800	- -	4187,95	,070	1,107	1,177
4900	- -	4287,95	,070	1,105	1,175
5000	- -	4387,95	,070	1,103	1,172
5100	- -	4487,95	,069	1,100	1,169

Oil

Oil of vitriol.	Acid.	Water.	Accrued density	Mathemat. sp. gravity.	
Grains.					
5200	– –	4587,95	,069	1,098	1,167
5300	– –	4687,95	,069	1,096	1,165
5400	– –	4787,95	,069	1,094	1,163
5500	– –	4887,95	,068	1,092	1,160
5600	– –	4987,95	,067	1,091	1,158
5700	– –	5087,95	,067	1,089	1,156
5800	– –	5187,95	,067	1,087	1,154
5900	– –	5287,95	,065	1,086	1,151
6000	– –	5387,95	,064	1,084	1,148
6100	612,05	5487,95	,064	1,082	1,146
6200	– –	5587,95	,063	1,081	1,144
6300	– –	5687,95	,062	1,080	1,142
6400	– –	5787,95	,062	1,078	1,140
6500	– –	5887,95	,061	1,077	1,138
6600	– –	5987,95	,060	1,076	1,136
6700	– –	6087,95	,060	1,074	1,134
6800	– –	6187,95	,060	1,072	1,132
6900	– –	6287,95	,060	1,070	1,130
7000	– –	6387,95	,059	1,069	1,128

With regard to the nitrous acid, I found alſo I had been a little too precipitate as to the time of examining its denſity after it had been mixed with water. Hence, making uſe of ſome whoſe ſpecific gravity was 1,474, I allowed the mixtures to reſt twelve hours, until it was diluted with twice its weight of water, and the ſubſequent mixtures ſix hours at leaſt; by the former proceſs of reaſoning, I found the ſpecific gravity of the mere nitrous acid to be 5,530.

Spirit

Spirit of nitre.	Acid.	Water.	Accrued denfity.	Mathemat. fp. gravity.	Phyfical fp. gravity.
900	– –	507	– –	1,557	1,557
1000	– –	607	– –	1,474	1,474
1100	– –	707	,035	1,413	1,448
1200	– –	807	,056	1,367	1,423
1300	– –	907	,065	1,329	1,394
1400	– –	1007	,065	1,298	1,363
1500	– –	1107	,077	1,273	1,350
1600	– –	1207	,082	1,251	1,333
1700	– –	1307	,082	1,233	1,315
1800	– –	1407	,083	1,217	1,300
1900	– –	1507	,083	1,204	1,287
2000	– –	1607	,096	1,191	1,269
2100	– –	1707	,088	1,181	1,254
2200	– –	1807	,071	1,176	1,247
2300	– –	1907	,068	1,162	1,230
2400	– –	2007	,068	1,154	1,222
2500	– –	2107	,067	1,147	1,214
2600	– –	2207	,065	1,141	1,206
2700	– –	2307	,063	1,135	1,198
2800	– –	2407	,061	1,129	1,190
2900	– –	2507	,058	1,124	1,182
3000	– –	2607	,055	1,120	1,175
3100	393	2707	,054	1,116	1,170
3200	– –	2807	,054	1,111	1,165
3300	– –	2907	,053	1,108	1,161
3400	– –	3007	,052	1,104	1,156
3500	– –	3107	,050	1,101	1,151
3600	– –	3207	,048	1,098	1,146
3700	– –	3307	,047	1,095	1,142
3800	– –	3407	,045	1,092 or 3	1,137
3900	– –	3507	,043	1,089	1,132
4000	– –	3607	,040	1,087	1,127
4100	– –	3707	,037	1,085	1,122
4200	– –	3807	,035	1,083	1,118
4300	– –	3907	,034	1,080	1,114
4400	– –	4007	,032	1,078	1,110
4500	– –	4107	,029	1,077	1,106
4600	– –	4207	,027	1,075	1,102
4700	– –	4307	,025	1,073	1,098
4800	– –	4407	,022	1,072	1,094
4900	– –	4507	,020	1,070	1,090
5000	– –	4607	,018	1,068	1,086
5100	– –	4707	,015	1,067	1,082
5200	– –	4807	,012	1,066	1,078
5300	– –	4907	,008	1,066	1,074

The foregoing experiments were made at the temperature of between 50 and 60° of FAHRENHEIT; but as it may be suspected, that the density of the above acids is considerably altered at degrees of temperature considerably different, I endeavoured to find the quantity of this alteration, and to calculate what this density would be at 55°, that the quantities of acid and water may thereby be investigated.

To this end I took some dephlogisticated spirit of nitre, and examined its specific gravity at different degrees of heat, and found it as follows:

	Deg.		Sp. gravity.
at	30	-	1,4653
	46	-	1,4587
	86	-	1,4302
	120	-	1,4123

Therefore, the total expansion of this spirit of nitre from 30 to 120°, that is, by 90° of heat, was 0,0527; for 1,4650 − 1,4123 = ,0527, by which we see that the dilatations are nearly proportional to the degrees of heat: for beginning with the first dilatation from 30 to 46°, that is, by 16° of heat ∻ 90 . 0,0527 :: 16 . 0,0093; but in reality these 16° of heat afforded a dilatation equal only to 0,0063; for 1,4650 − 1,4587 = 0,0063; so that the difference betwixt the calculated and observed dilatations is only $\frac{30}{10000}$, a difference of no consequence in the present case, and that might arise from the immersion of the cold glass ball filled with mercury in the liquor, it being the solid I use to try the specific gravity of liquids. In the next case the difference is still less; for ∻ 90 . 0,0527 :: 56 . 0,0327; but 56° of heat produced in reality a dilatation of 0,0348 for 1,4650 − 1,4302 = 0,0348, so that the calculation is deficient only in $\frac{21}{10000}$.

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I afterwards tried another, and somewhat stronger, spirit of nitre, whose specific gravity was

	Deg.		Sp. gravity.
at	34	-	1,4750
	49	-	1,4653
	150	-	1,3792

Here also the expansions are nearly proportional to the degrees of heat; for 116° of heat (the difference between 34 and 150) produce an expansion of 0,0958; and 15° of heat (the difference between 34 and 49) produce an expansion of 0,0097, and by calculation 0,0123, which last differs from the truth only by $\frac{26}{10000}$.

By this experiment we see, that the stronger the spirit of nitre is, the more it is expanded by the same degree of heat: for if the spirit of nitre of the last experiment were expanded in the same proportion as in the first, its dilatation by 116° of heat should be 0,0679, whereas it was found to be 0,0958.

As the dilatation of spirit of nitre is far greater than that of water by the same degree of heat, and as it consists only of acid and water, it clearly follows, that its superior dilatability must be owing to the acid part; and hence, the more acid is contained in a given quantity of spirit of nitre, the greater is its dilatability. We might therefore suppose, that the dilatation of spirit of nitre was intermediate betwixt that of the quantity of water it contains and that of its quantity of acid; but there exists another power also which prevents this simple result, namely, the mutual attraction of the acid and water to each other, which makes them occupy a less space than the sum of their joint volumes, which condensation I have therefore called their *accrued density*. Taking this into the account,

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we may conſider *the dilatation of ſpirit of nitre as equal to thoſe of the quantities of water and acid it contains minus the condenſation they acquire from their mutual attraction*, *and this rule holds as to all other heterogeneous compounds.*

To find the quanties of acid and water in ſpirit of nitre, whoſe ſpecific gravity was found in degrees of temperature different from thoſe for which the table was conſtructed, *viz.* 54, 55, or 56° of FAHRENHEIT, the ſureſt method is to find how much that ſpirit of nitre is expanded or condenſed by a greater or leſſer degree of heat, and then, by the rule of proportion, find what its denſity would be at 55°; but if this cannot be done, we ſhall approach pretty near the truth, if we allow $\frac{10}{1000}$ for every 15° of heat above or below 55° of FAHRENHEIT, when the ſpecific gravity of ſpirit is between 1,400 and 1,500; and $\frac{8}{1000}$ when the ſpecific gravity is between 1,400 and 1,300.

As to oil and ſpirit of vitriol I found the dilatations exceeding irregular, probably by reaſon of a white foreign matter, which is more or leſs ſuſpended or diſſolved in it, according to its greater or leſſer dilution. This matter I would not ſeparate, as I intended trying the denſity of this ſubſtance in the ſtate in which it is commonly uſed. In general I found, that 15° of heat cauſe a difference of about $\frac{8}{1000}$ in its ſpecific gravity when it exceeds 1,800; and of $\frac{3}{1000}$ when its ſpecific gravity is between 1, 400 and 1,300, its dilatation is greater than that of water, and ſo much greater as it is ſtronger.

The dilatations of ſpirit of ſalt are very nearly proportional to the degrees of heat, as appears by the following table.

	Deg.		Sp. gravity.
at	33	-	1,1916
	54	-	1,1860
	66	-	1,1820
	128	-	1,1631

Hence $\frac{6}{1000}$ ſhould be added or ſubtracted for every 21° above or below 55° in order to reduce it to 55°, the degree for which its proportion of acid and water was calculated. The dilatability of this acid is much greater than that of water, and even than that of the nitrous acid of the ſame denſity.

I now proceed to examine the quantity of pure acids taken up at the point of ſaturation by the various ſubſtances they unite with.

OF THE MINERAL ALKALI.

That which I made uſe of was procured from Mr. TURNER, who by a peculiar and ingenious proceſs extracts it in the greateſt purity form common ſalt.

Of this alkali I rendered a portion tolerably cauſtic in the uſual manner, and evaporating 1 oz. of the cauſtic ſolution to perfect dryneſs, I found it to contain 20,25 gr. of ſolid matter. I was aſſured, that the watery part alone exhaled during the evaporation, as the quantity of fixed air contained in it was very ſmall, and to diſſipate this a much greater heat would be requiſite than that which I uſed. This dry alkali I immediately diſſolved in twice its weight of water, and ſaturating it with dilute vitriolic acid, found it to contain 2,25 gr. of fixed air, that being the weight which the ſaturated ſolution

lution wanted of being equal to the joint weights of the water, alkali, and spirit of vitriol employed.

The quantity of mere vitriolic acid necessary to saturate 100 gr. of pure mineral alkali I found to be 60 or 61 gr. the saturated solution, thus formed, being evaporated to perfect dryness weighed 36,5 gr.; but of this weight only 28,38 were alkali and acid, therefore the remainder, that is, 8,12 gr. were water. Hence, 100 gr. of GLAUBER's salt, perfectly dried, contain 29,12 of mere vitriolic acid, 48,6 of mere alkali, and 22,28 of water; but GLAUBER's salt cryſtallized contains a much larger proportion of water; for 100 gr. of these crystals being heated red-hot lost 55 gr. of their weight. This loss I suppose to arise merely from the evaporation of the watery part, and the remaining 45 contained alkali, water, and acid, in the same proportion as the 100 gr. of GLAUBER's salt, perfectly dried, abovementioned; then these 45 contained 13,19 gr. of vitriolic acid, 21,87 of fixed alkali, and 9,94 of water; consequently 100 gr. of crystallized GLAUBER's salt contain 13,19 of vitriolic acid, 21,87 of alkali, and 64,94 of water.

I also saturated this alkali with the dephlogisticated nitrous acid, and found that 100 gr. of the alkali took up 57 of the mere nitrous acid in the experiment I most depended on; but this quantity varied in some experiments a few grains, being sometimes 60, and sometimes 63 gr.; so that I conclude the proportion of this acid, taken up by the alkali, is nearly the same as that of the vitriolic acid. Supposing this quantity to be 57 gr. then 100 gr. Cubic nitre, perfectly dry, contain 30 of acid, 52,18 of alkali, and 17,82 of water; but Cubic nitre crystallized contains something more water; for 100 gr. of these crystals lose about 4 by gentle drying; therefore 100 gr.

of

of the cryſtallized ſalt contain 28,8 of acid, 50,09 of alkali, and 21,11 of water.

Of mere marine acid, 100 gr. of this alkali required from 63 to 66 or 67 gr.; perhaps one reaſon of this variety is, that it is exceeding hard to hit the true point of ſaturation. Allowing it to be 66 gr. then 100 gr. of perfectly dry *common ſalt* contain nearly 35 of real acid, 53 of alkali, and 13 of water; but 100 gr. of the cryſtallized ſalt loſe 5 by evaporation; then 100 gr. of theſe cryſtals contain 33,3 of acid, 50 of alkali, and 16,7 of water.

The proportion of fixed air, alkali, and water, in cryſtallized mineral alkali, I inveſtigated thus: 200 gr. of theſe cryſtals were diſſolved in 240 of water; the ſolution was ſaturated by ſuch a quantity of ſpirit of nitre as contained 40 of mere nitrous acid; hence I inferred, that theſe 200 gr. of alkali contained 70 of real alkali. The ſaturate ſolution weighed 40 gr. leſs than the ſum of its original weight, and that of the ſpirit of nitre added to it; therefore it loſt 40 gr. of fixed air. The remainder, therefore, of the original weight of the cryſtals muſt have been water, that is, 90 gr.; conſequently 100 gr. of theſe cryſtals contained 35 of alkali, 20 of fixed air, and 45 of water.

This proportion is, particularly with regard to the alkali, very different from that found by Mr. BERGMAN and LAVOISIER, which I impute to their having uſed ſoda recently cryſtallized. Mine had been made ſome months, and probably loſt much water and fixed air by evaporation, which altered the proportion of the whole. According to the calculation of theſe philoſophers 100 gr. of this alkali takes up 80 of fixed air.

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The ſpecific gravity of the cryſtallized mineral alkali weighed in æther I found to be 1,421.

OF THE VOLATILE ALKALI.

It is not poſſible by the old chymical methods to find the proportion of the ingredients in volatile alkalies, whether in a liquid or in a concrete ſtate; ſeeing that, though it may be ſeparated from fixed air, yet it cannot from water, on account of its extreme volatility. Then to find this proportion we muſt recur to the experiments of Dr. PRIESTLEY, who by his new analyſis produced this alkali free from the aërial acid and water in the form of air: and in the third volume of his Obſervations, p. 294. informs us, that $1\frac{6}{7}$ meaſures of alkaline air take up, and are ſaturated by, 1 meaſure of fixed air. Let us ſuppoſe the meaſure to contain 100 cubic inches; then 185 cubic inches of alkaline air take up 100 of fixed air; but 185 cubic inches of alkaline air weigh, at a medium, 42,55 gr.; and 100 cubic inches of fixed air weigh 57 gr.; then 100 gr. of pure volatile alkali, free from water, take up 134 of fixed air.

On expelling its aërial acid from a parcel of this alkali in a concrete ſtate, and formed by ſublimation, I found 100 gr. of it to contain 53 of fixed air, and therefore, according to the preceding reaſoning, 39,47 of real alkali and 7,53 of water *per cent*.

Saturating a ſolution of this alkali with the vitriolic, nitrous, and marine acids, I found, that 100 gr. of the mere alkali take up 106 of mere vitriolic acid, 115 of the nitrous, and 30 of the marine.

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The ſpecific gravity of the concrete volatile alkali weighed in æther was 1,4076.

The proportion of water in the different ammoniacal ſalts I have not been able to find, on account of their volatility; but believe it to be very ſmall, as volatile alkali and fixed air cryſtallize without the help of water, when both are in an aërial ſtate.

OF CALCAREOUS EARTH.

I firſt diſſolved this earth in the nitrous acid, and found that, after allowing for the loſs of fixed air and the quantity of water I formerly mentioned, 100 gr. of the pure earth take up 104 of mere nitrous acid. Inſtead of diſſolving this earth immediately in the vitriolic acid, I precipitated its ſolution in the nitrous by the gradual addition of the vitriolic, and found that to effect this 91 or 92 gr. only of mere vitriolic acid were required.

100 gr. of this pure earth demand for their ſolution 112 of mere marine acid. The ſolution, which is at firſt colourleſs, grows greeniſh on ſtanding. Natural Gypſum varies in its proportion of acid, earth, and water, 100 gr. of it containing from 32 to 34 of acid, and alſo of earth, and from 26 to 32 of water. The artificial contains 32 of earth, 29,44 of acid, and 38,56 of water; when well dried it loſes about 24 of water, and therefore contains 42 of earth, 39 of acid, and 19 of water *per cent.*

100 gr. *nitrous ſelenite*, carefully dried, contain 33,28 of acid, 32 of earth, and 34,72 of water.

100 gr. *marine ſelenite*, well dried, ſo as to loſe no part of the acid, contain 42,56 of acid, 38 of earth, and 19,44 of water.

OF

OF MAGNESIA OR MURIATIC EARTH.

This earth, perfectly dry and free from fixed air, could not be diſſolved in any of the acids without heat. In the temperature of the atmoſphere even the ſtrongeſt nitrous acid did not act upon it in twenty-four hours; but in a heat of 180° theſe acids diluted with four or ſix times their quantity of water attacked it very ſenſibly; but as much of the acids is diſſipated by heat, I could not judge of the exact quantity of acid requiſite to diſſolve a given quantity of it, any otherwiſe than by precipitating the ſolutions by another ſubſtance, whoſe capacity for taking up acids was known. The ſubſtance I uſed was a tolerably cauſtic vegetable alkali. By this method I found, that 100 gr. of pure magneſia take up 125 gr. of mere vitriolic acid, 132 of the nitrous, and 140 of the marine. None of theſe ſolutions reddened vegetable blues; all of them appeared to contain ſomething gelatinous; that in the marine acid became greeniſh on ſtanding for ſome time.

100 gr. of perfectly dry Epſom ſalt contain 45,67 of mere vitriolic acid, 36,54 of pure earth, and 17,83 of water; but 100 gr. of cryſtallized Epſom loſe 48 by drying, and conſequently contain 23,75 of acid, 19 of earth, and 57,25 of water. Common Epſom ſalt contains an exceſs of acid, for its ſolution reddens vegetable blues.

100 gr. of nitrous Epſom, well dried, contain 35,64 of acid, 27 of pure earth, and 37,36 of water.

The ſolution of marine Epſom cannot be tolerably dried without loſing much of its acid, together with the water.

The ſpecific gravity of pure muriatic earth is 2,3296.

 OF

OF EARTH OF ALLUM OR ARGILLACEOUS EARTH.

This earth I found to contain about 26 *per cent.* of fixed air, though I had previouſly kept it red-hot for half an hour: this ſurpriſed me much, as moſt writers ſay it contains ſcarce any. It diſſolved in acids with a moderate effervescence until the heat was raiſed to 220°, after which I found the ſolution lighter than the quantities employed in the proportion I mentioned.

100 gr. of this earth (excluſive of the fixed air) require 133 of the *mere* vitriolic acid to diſſolve them. This ſolution I made in a very dilute ſpirit of vitriol, whoſe ſpecific gravity was 1,093, in which the proportion of acid to that of water was nearly as 1 to 14. This ſolution contained a ſlight exceſs of acid, turning vegetable blues into a browniſh red; but it cryſtallized when cold, and the cryſtals were of the form of allum; ſo that I believe this to be nearly the proper proportion of its acid and earth; but there was not water enough to form large cryſtals. As this ſolution contained an exceſs of acid, I added more earth to it, but could not prevent its tinging blue paper red, until it formed an inſoluble ſalt, that is, one that required an exceeding large quantity of water to diſſolve it, and while part was thus become inſoluble, yet another part would ſtill retain an exceſs of acid; ſo that at the ſame time part would be ſuperſaturated with earth, and another with acid, if tinging vegetable blues be a mark of an exceſs of acidity, which indeed in this caſe ſeems dubious.

100 gr. of Allum, perfectly dried, contain 42,74 of acid, 32,14 of earth, and 25,02 of water; but cryſtallized allum loſes 44 *per cent* by deſiccation; therefore 100 gr. of it contain 23,94 acid, 18 of earth, and 58,06 of water.

100 gr. of this pure earth take up as far as I can judge 153 of the mere nitrous acid. The solution still reddened vegetable blues; but after the addition of this quantity of pure earth, I think it was, that an insoluble salt came to be formed. The solution, when cold, grew turbid, and could not be wholly dissolved by 500 times its weight of water.

The same quantity of pure earth requires 173,45 of the mere marine acid for its solution; but the solution still reddens vegetable blues. After this an insoluble salt was formed; but the beginning of its formation is difficultly discovered both in this and in the former cases.

The specific gravity of argillaceous earth, containing 25 *per cent.* of fixed air, I found to be 1,9901.

OF PHLOGISTON.

Before I proceed to investigate its proportion in various compounds, and particularly in phlogisticated acids, it will be necessary to say something of its nature.

It is allowed on all hands, that fixed air, or the Aërial Acid, as it is more properly called, is capable of existing in two states; the one fixed, concrete, and unelastic, as when it is actually combined with calcareous earth, alkalies, or magnesia; the other, fluid, elastic, and aëriform, as when it is actually disengaged from all combination. In its concrete and unelastic state it can never be produced single and disengaged from other substances; for the moment it is separated from them, it assumes its aërial and elastic form. The same thing may be said of phlogiston: it can never be produced in a *concrete state*, single and uncombined with other substances; for the instant it

is diſengaged from them, it appears in a fluid and elaſtic form, and is then commonly called *inflammable air*. Theſe different ſtates of the ſame ſubſtance ariſe, according to the immortal diſcoveries of Dr. BLACK, from the different portions of elementary fire contained in ſuch ſubſtance, and abſorbed by it, whilſt its ſenſible heat remains the ſame, and hence called its *ſpecific fire*. For want of attention to theſe different ſtates, the very exiſtence of phlogiſton as a diſtinct principle has been frequently called in queſtion, and chemiſts have been required to exhibit it ſeparate in its fixed ſtate, without recollecting, that neither can fixed air be ſhewn ſeparate in a concrete ſtate, nor that phlogiſton may alſo be in the ſame predicament; while others have totally miſtaken the nature of inflammable air, and imagined it to be a combination of acid and phlogiſton. The reaſon why fixed air cannot be ſeparated from any ſubſtance in a concrete ſtate is, becauſe when it is ſeparated, for inſtance by means of an acid, there is always a double decompoſition, the acid yielding its ſpecific quantity of fire to the concrete fixed air, which then aſſumes an aërial form, while the fixed air yields the ſubſtance it was combined with to the acid. This is ſo true, that though a ſolution of lime in the nitrous acid yields a conſiderable quantity of heat, yet a ſolution of chalk in that acid ſcarcely yields any; for all the fire that is ſet looſe, and rendered ſenſible in the firſt caſe, is abſorbed by the fixed air in the ſecond caſe, being preciſely that which converts it into an aërial form. The ſeparation of phlogiſton from a metallic earth in the form of inflammable air ariſes from the ſame cauſe, the diſſolving acid yielding its fire to the phlogiſton, which then aſſumes an aërial form, while the phlogiſton yields the metallic earth to the acid. It is true, that much ſenſible heat is produced on this occaſion, for which

three

three substantial reasons may be assigned; first, the proportion of fixed air in a given weight of crude calcareous earth, is much greater than that of phlogiston in any metal, as will hereafter be shewn, it being in the former one-third of the whole, and that of phlogiston in the latter for the most part not even one-sixth. Secondly, much of the phlogiston combines with the acid itself during the solution, and expels part of its specific quantity of fire, as Dr. CRAWFORD has shewn, and as I have since experienced; and this fire must occasion sensible heat. Thirdly, much of the phlogiston, during solution, unites to the surrounding atmosphere, expelling also part of its specific fire, and this also must occasion sensible heat; and hence it is, that metallic solutions *in vacuo* are generally attended with less heat, though with a more violent effervescence than in open air. The solution of metallic calces is not attended with as much heat as that of their respective metals, not only because neither the dissolving acids nor the surrounding air is much phlogisticated; but also because they contain an elastic fluid in a concrete state, which absorbs much of the fire given out by the dissolving acids, as it acquires an aërial state.

The origin and formation of inflammable air being thus explained, I now proceed to shew its identity and homogeneity with phlogiston. By phlogiston is generally understood that principle in combustible bodies on which their inflammability principally depends; that principle to which metals owe their malleability and splendor; that which combined with vitriolic acid forms sulphur; that which diminishes respirable air. Now inflammable air is that very principle which alone is truly inflammable, as Mr. VOLTA has elegantly shewn. In effect, combustible substances are either animal or vegetable,

as horns, hair, greaſe, wood, &c.; from all of which Dr. HALES has extracted inflammable air; or charcoal, from which Mr. FONTANA has extracted it, as did Dr. PRIESTLEY from reſins, ſpirit of wine, and æther, in all which it is the only principle that is inflammable, and they are inflammable only in proportion as they yield it; or phoſphorus, from whoſe acid Dr. PRIESTLEY has obtained this air by means of minium, for it was the acid, and not the minium, that contained it, as Dr. PRIESTLEY rightly conjectured, the acid obtained by deliqueſcence being never thoroughly dephlogiſticated until heated and vitrified, as Mr. MARGRAAF has ſhewn; or they are mineral ſubſtances, as ſulphur, from which inflammable air has been ſeparated by means of fixed alkalies, and, according to Dr. PRIESTLEY, alſo by means of marine air, or bitumens or bituminous ſubſtances, all of which may be made to yield it; or metallic ſubſtances, as zinc and regulus of arſenic, both of which are inflammable; but neither of them is ſo when deprived of its inflammable air: this is, therefore, the true and only principle of inflammability in any ſubſtance. I acknowledge that the inflammable air, proceeding from almoſt all theſe ſubſtances, is exceeding impure; that it contains from ſome a mixture of aërial acid or of oil, and from all ſome part of the ſubſtance which yields it or expels it, and hence its ſmell is different, according to the claſs of the ſubſtances from which it is extracted; but it is equally true, that none of theſe ſubſtances contribute to its inflammability; on the contrary, it is ſo much the leſs inflammable (that is, requires ſo much more air to be mixed with it before it flames) as it contains more of theſe heterogeneous ſubſtances. Hence inflammable air of the moraſſes is never totally conſumed*; and, on the contrary,

* 15 Roz. 146.

inflam-

inflammable air, from metals which is the pureſt of all, is alſo the moſt inflammable.

Secondly, Inflammable air is alſo the principle which reduces metallic earths to a metallic ſtate, and gives them their metallic ſplendor. This has been proved analytically and ſynthetically, and therefore may be ſaid to be as completely demonſtrated as any thing in natural philoſophy: thus Dr. PRIESTLEY has extracted inflammable air from iron and zinc by heat alone; and the iron, thus ſtripped of its phlogiſton, loſt its ſplendor, and was of a black colour, which is that which iron, ſlightly dephlogiſticated, always aſſumes, as appears by *martial æthiops*: ſo alſo zinc and regulus of arſenic, when once inflamed, loſe their metallic appearance: ſo alſo a mixture of lead and tin inflames in a moderate heat, and then both are converted into a calx deſtitute of ſplendor and malleability. On the other hand, if a current of inflammable air, in the act of combuſtion, be directed on the calces of iron, lead, or mercury, they are immediately revived and reſtored to their metallic form, as appears by the experiment of Mr. CHAUSSIER *. The following experiment is ſtill more concluſive: if a poliſhed plate of iron be put into a ſaturate and dilute ſolution of copper in the vitriolic or marine acids (I mention theſe becauſe they are commonly uſed for the production of inflammable air, though the reſult is the ſame when other acids are uſed), no effervеſcence will ariſe, no inflammable air will be caught; but the iron will be diſſolved, and the copper precipitated in its metallic form. Here inflammable air muſt be produced as uſual, for the acid quits the copper and diſſolves the iron; but this inflammable air inſtantly loſes its aërial form, and unites to the copper, juſt as fixed air leaves alkalies to unite to lime

* 10 Roz. 313.

without

without any effervefcence; and by this fame inflammable air is the copper evidently reduced, acquiring fplendor, malleability, and every other metallic property. But if the folution of copper be not faturated with copper, a fmall quantity of inflammable air may be caught, as the excefs of acid will difengage more of it from the iron than the calx of copper can take up. Inflammable air is then the principle that metallizes metallic earth; and if metals contain only a fpecific earth and phlogifton, inflammable air certainly contains nothing elfe but phlogifton. If iron and the arfenical acid be digefted together, no inflammable air is produced; but the arfenical acid is, in great meafure, converted into white arfenic, as Mr. BERGMAN has obferved, and alfo Mr. SCHEELE *; what reafon can be affigned why inflammable air is not produced by this as well as by all other acids; but that this metallic acid received it, and was by it reduced to a femi-metallic form, as by pure phlogifton? Yet this acid produces inflammable air, from zinc becaufe zinc gives out more phlogifton than the regulus of arfenic can take up; but it attracts and is metallized by a part of it, and it is only the excefs that appears in the form of inflammable air, as Mr. SCHEELE has remarked. This inflammable air, indeed, is not pure, for it holds fome of the regulus in folution; but this portion of regulus does not enter into its compofition, as is very evident.

Thirdly, Inflammable air is the fubftance which, with vitriolic acid, forms fulphur, for it is the very fubftance which the vitriolic acid feparates from metals; and this fubftance, fo feparated, when in fufficient quantity, and in proper circumftances, unites to it in fuch proportion as to form common fulphur. Thus fulphur is formed by diftilling concentrated vitriolic acid

* 2 Nov. Act. Upfal. p. 210. Kon. Veten. Accad. Handlingar, vol. 36. p. 288.

with

with iron or bismuth, or by distilling tartar vitriolate with regulus of antimony. It is this also that diminishes respirable air, as Dr. PRIESTLEY has clearly shewn in the 5th vol. of his Observations, p. 84.; for though in its complete aërial state, after it has absorbed that large quantity of fire requisite to its aërial form, it difficultly and slowly unites to respirable air in the heat of the atmosphere, their points of contact through their difference of density being very small, and there being no substance at hand to receive the large portion of elementary fire they both contain, and of which they must lose a large proportion before they can combine together; yet while inflammable air is (as Dr. PRIESTLEY elegantly expresses it) in its *nascent* state, before it acquires its whole quantity of specific fire, respirable air easily unites to it, and is diminished in proportion to its purity; but if to a mixture of both, igneous particles of sufficient density to be visible be introduced, a degree of heat is excited, which, as it rarifies the dephlogisticated part of respirable air to a greater degree than it can inflammable air *, brings both into nearer contact, increases their attraction to each other, and both uniting give out their fire, or in other words *inflame*, when in proper proportion to each other, without any decomposition of either, unless the loss of a great part of their specific fire be called a decomposition, which loss is not usually called a decomposition; for water is never said to be decomposed when it becomes ice, nor metals when they become solid on cooling.

In answer to all this it will be said, that inflammable air undoubtedly contains phlogiston, which produces all the before-mentioned effects; but that the phlogiston it contains is united to some other substance, which some will have to be an acid,

* 5 PRIEST. 359.

 some

ſome an earth, and others reſpirable air. To theſe hypotheſes I ſhall oppoſe one general obſervation, which is, that ſince inflammable air, when pure, that is, when diſengaged from all heterogeneous ſubſtances which no way contribute to its inflammability, has always the ſame properties; it muſt, if it conſiſts of phlogiſton combined with any other ſubſtance, be always united to the ſame ſpecific ſubſtance; that is, if this be an acid, it muſt be always the ſame ſpecies of acid, or if an earth, it muſt be always the ſame ſpecies of earth; for we find, that ſubſtances, which are only *generically* the ſame, always produce, with any other given ſubſtance, compounds whoſe properties are very different from each other. Thus we ſee that the different ſpecies of alkalies, or earths, or metals, produce with one and the ſame ſpecies of acid compounds eſſentially different. This is a rule which, as far as I know, admits of no exception: and if we apply it to the abovementioned ſuppoſitions it will intirely deſtroy them; for it is impoſſible to think, that the phlogiſton can in every ſubſtance, that produces inflammable air, meet either the ſame acid, or earth, or any reſpirable air.

But to be more particular, the following reaſons demonſtrate that an acid of any ſort cannot be the baſis of inflammable air. 1ſt. Inflammable air has been, by Dr. PRIESTLEY, ſeparated from metals by mere heat. Now metals contain no acid, except perhaps their dephlogiſticated calx, which thoſe eminent chemiſts, BERGMAN and SCHEELE, ſuſpect to be of an acid nature; but theſe calces cannot enter into the compoſition of inflammable air, otherwiſe the inflammable air of each different metal would have different properties, as already ſhewn: nor indeed are theſe the acids that have been ſuppoſed to enter into the compoſition of inflammable air; but rather thoſe acids by

whose means it is extricated. But as this air is extricated from metals, not only by acids, but also by alkalies *, this supposition must vanish of course.

The same reasons militate with equal strength against the supposition that an earth of any kind enters into the composition of this air; nor is there an instance of any earth rendered permanently fluid by any means, except in sparry air. Besides, if it were a metallic earth, it must necessarily be supposed to be in a metallic state; and how then could it escape the action of all kind of acids? for no acid is capable of decompounding inflammable air. Lastly, respirable air cannot be said to be the basis of inflammable air, unless we suppose that respirable air enters into the composition of metals; for Dr. PRIESTLEY has, by solar heat, extracted inflammable air from them in a vessel full of mercury, into which respirable air had no access, and even *in vacuo*. Besides, respirable air and phlogiston form other compounds very different from inflammable air, *viz.* fixed and phlogisticated airs as will presently be seen.

It may also be fairly urged against all these suppositions, that they are not founded on any direct experiment, nor any known analogy, but merely gratuitous, or at least deduced from experiments inadequate to their support; whereas the opinion that inflammable air is nothing else than phlogiston thrown into a fluid form by elementary fire, is directly founded on that experiment whereby inflammable air is separated from metals by mere solar heat in the most perfect vacuum, just as fixed air united to marble and in a concrete state (in which it is nearly of equal density with gold) is separated from the marble, and thrown into a permanently fluid form by heat alone.

* Mem. Par. 1776, p. 687.

In favour of the exiſtence of an acid in inflammable air, it has been ſaid, that if this air be paſſed through water tinged blue by litmus, it reddens inſtantly. I have ſeen this frequently happen when inflammable air has been extracted from iron by ſpirit of vitriol; but if this air be waſhed, by paſſing it through lime-water, and then paſſed through, or agitated in, an infuſion of litmus, it will not diſcolour it in the leaſt: this I have ſeen done by Mr. FONTANA in June 1779. It has alſo been ſaid, that inflammable air and alkaline air, mixed together, form a cloud; but this has been fully diſproved by Dr. PRIESTLEY, in the fourth volume of his Obſervations.

That an earth of any kind is eſſentially requiſite to the conſtitution of inflammable air, ſeems to me utterly improbable; nor do I know of any experiment from whence it can be inferred. That metallic ſubſtances may be held in ſolution by inflammable air is certain; but it is equally ſo, that they no way contribute to its inflammability *, and are quite diſtinct from it.

But the opinion, that inflammable air conſiſts of reſpirable air ſuper-ſaturated with phlogiſton, is grounded on very ſpecious arguments drawn from experiments to be found in various part of Dr. PRIESTLEY's works, which deſerve ſo much the more attention as the facts mentioned by that excellent philoſopher are not to be queſtioned. I ſhall endeavour to ſtate them with accuracy; but ſhall at the ſame time accompany them with ſuch remarks as ſeem to me to invalidate the concluſion that has been drawn from them.

In the firſt volume of Dr. PRIESTLEY's Obſervations it appears, that a quantity of ſtrong inflammable air, having been agitated in a glaſs jar immerſed in a trough of water,

* 2 PRIESTLEY, 268.

the surface of which was exposed to the common atmosphere, after the operation had continued ten minutes near one-fourth of the quantity had disappeared; the remainder became fit for respiration, and yet was weakly inflammable. By further agitation it was diminished half, and then admitted a candle to burn in it though feebly; but, on continuing the agitation a little longer, it came to extinguish a candle. Upon this I shall remark, first, that it clearly follows, from this experiment, that if the external respirable air had no access to the inside of the jar, half nearly of the inflammable air was converted into, or consisted of, respirable air, since such quantity of air was found in it after the operation. Now it is absolutely impossible that either could happen; for inflammable air could not be converted into half nor even one-third or one-fourth of its volume of respirable air, as even one-fourth of respirable air contains more matter than four times its bulk of inflammable air; it is then evident, that the external air must have had access to it. Secondly, I agitated about half a pint of inflammable air, obtained from iron and previously passed through lime-water and kept over mercury, in about twelve times its bulk of water, out of which its air had been boiled in a glass bottle closed with a glass-stopper. The agitation continued at several times at least two hours. A large quantity of the air was indeed absorbed, as appeared by opening the bottle in water; but the remainder appeared, by the nitrous test, as noxious, and was also found to be as inflammable as at first. Even Dr. PRIESTLEY attests, that inflammable air, which had been united to water for one month, was afterwards as inflammable as ever 3 PR. 267.

The true explanation of the first experiment appears, therefore, to be the following: First, Water easily imbibes inflammable air, but does not combine with it; for after it has imbibed

bibed one-fourteenth of it, its taſte is no way altered, as Dr. PRIESTLEY has obſerved. I PR. 196. Water alſo eaſily imbibes common air: when, therefore, inflammable air is agitated in water having a communication with the atmoſphere, the inflammable air muſt neceſſarily be diminiſhed by reaſon of its abſorbtion, and the part ſo abſorbed immediately eſcapes out of the water into the atmoſphere, as is evident by the ſmell which is perceived when the quantity of inflammable air is conſiderable. This eſcape gives room for the further abſorbtion of the inflammable air which then eſcapes in the ſame manner. In the mean time the common air under the jar riſes into it, as appears by the direct experiments both of Dr. PRIESTLEY * and Mr. FONTANA; and hence the air in the jar muſt appear by the nitrous ſlightly phlogiſticated and reſpirable; but a further agitation will decompoſe the common air, as we ſhall ſoon ſee, and then a candle will be extinguiſhed. The ſame proceſs takes place when inflammable air ſtands long in water whoſe ſurface is expoſed to the atmoſphere.

Another experiment of the ſame tendency, but ſeemingly more deciſive, is to be found in the 4th vol. of Dr. PRIESTLEY's Obſervations, p. 368. There it is related, that a portion of inflammable air, incloſed in a glaſs tube, hermetically ſealed and heated until the glaſs was ſoftened, ſtained the glaſs black, and the tube being opened, the air was found reduced to one-third of its bulk; and this reſiduum was found to be mere *phlogiſticated air*, neither precipitating lime-water, nor being affected by nitrous air, or in the leaſt inflammable. Yet deciſive as this experiment appears, a little conſideration will ſhew the abſolute impoſſibility that inflammable air ſhould conſiſt of one-third phlogiſticated air and two-thirds phlogiſton;

* I PR. 96. 159. 3 PR. 156. Phil. Tranſ. 1779, p. 443.

for,

for, in the firſt place, one Cubic inch of phlogiſticated air weighs 0,377 of a grain: now let us ſuppoſe, that to this phlogiſticated air is added two-thirds of its bulk of phlogiſton; and to make the ſuppoſition ſtill ſtronger, let us alſo ſuppoſe, that phlogiſton has no weight; then, by the ſuppoſition, this compound of phlogiſticated air and phlogiſton will conſtitute inflammable air, and amount to a bulk of three Cubic inches, and theſe three Cubic inches will weigh no more than 0,377 of a grain; but if three Cubic inches of inflammable air weigh 0,377 of a grain, one Cubic inch ſhould weigh 0,105 of a grain, which cannot be; for then inflammable air would be little more than one-third lighter than common air, contrary to all the experiments that have been hitherto made, and particularly thoſe of Mr. CAVENDISH, FONTANA, and Dr. PRIESTLEY himſelf, which ſhew it to be about eleven times lighter than common air. Secondly, It is ſaid, that the matter which ſtained the glaſs black was the true phlogiſtic part of inflammable air, and was afterwards ſeparated by means of minium. This then contained no phlogiſticated air; but is it not certain, that if there had been enough of it, the minium would have been reduced and converted into lead? And might not inflammable air be again ſeparated from that lead, though no phlogiſticated or common air were at hand to ſupply its other ſuppoſed conſtituent part? Thirdly, In one of Dr. PRIESTLEY's experiments the inflammable air, contained in the glaſs tube which was moſt heated, was reduced to ſo ſmall a bubble that no experiment could be made on it: therefore, in this, at leaſt, the quantity of phlogiſticated air did not amount to one-third, but was quite inconſiderable; the remainder then being taken up by the calx of lead in the glaſs, was pure mere phlogiſton, ſo that this experiment is a ſtrong proof of my opinion.

Fourthly,

Fourthly, If phlogiſton could be decompoſed by heat, and then leave a reſiduum of phlogiſticated air, amounting to one-third of its bulk, the diminution ariſing from its inflammation with common or dephlogiſticated air could never be ſo great as it is found to be by repeated experiments; for when inflammable and common air are fired in the proportion of eleven of the latter to four of the former, a bulk equal to the whole of the inflammable air, and to one-fifth of the common air, diſappears, according to Mr. VOLTA *, and the diminution is about two-fifths of the whole, or more exactly out of fifteen meaſures, only 8,8 remain; but if the inflammable air were decompoſed, and one-third of it, being phlogiſticated air, ſhould remain, then not quite one-fifth of the whole would vaniſh, and the reſiduum ſhould be 10,54 meaſures. This evidently proves, that pure inflammable air is never decompoſed (unleſs the loſs of its fire be called a decompoſition); but in the act of inflammation is totally transferred upon the pure part of reſpirable air to which it unites. Fifthly, To obtain ſtill a clearer inſight into this matter, I intreated Mr. CAVALLO, who is very expert in the management of the blow-pipe, as well as in pneumatic experiments, to repeat this experiment in my laboratory. We accordingly filled a tube 10,5 inches long, and one-fourth of an inch in diameter, with inflammable air from iron received over mercury, and having made the tube red-hot throughout and black, and ſoftened it ſo far as to endanger the eſcape of the air, we opened it on mercury. The air was diminiſhed only one-tenth, and inflamed with an exploſion as loud as an equal quantity of the ſame inflammable air that had not been heated.

* Roz. April 1779, p. 295.

The

The only question that remains then is, whence the phlogisticated air proceeded which Dr. PRIESTLEY mentions to have found? The circumstance of his experiment would furnish a plausible answer; but the doctor has lately informed me, that he believes the air was really inflammable, but being a very small quantity escaped before the flame could be applied.

It seems, therefore, sufficiently proved, that inflammable air purified from the acids or other substances that expel it from its basis, and also from all particles of the body to which it was originally united, such as inflammable air from metals received on mercury, and well washed in lime-water, is one and the same substance with phlogiston, differing only in quantity of fire, inflammable air containing nearly the same quantity of this element as the same bulk of atmospheric air, as Dr. CRAWFORD has found by some late experiments, an account of which will soon be laid before the public. This does not contradict that most important discovery of this ingenious philosopher, that fire and phlogiston repel each other: the meaning of this being only, that the addition of phlogiston to any substance, as to respirable air, dephlogisticated acids, metallic calces, expels part of the fire already contained in such substance; and, on the contrary, by the removal of phlogiston from any substance, the quantity of fire absorbed by such substance is increased.

It may appear extraordinary, supposing inflammable air and phlogiston to be the same substance, that inflammable air should mix so easily with water, whereas phlogiston constantly repels and is repelled by it; but this intirely depends on the state of this same substance, which, when fixed and concrete, is called *phlogiston*, and, when rarified and aëriform, *inflammable air*. In this latter state it mixes with water in proportion to its rare-

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faction, as it even does in the leſs denſe forms of its concrete ſtate: thus æther is totally abſorbed by ten times its weight of water. The animal oil of Dippel mixes intirely with water; ſo does pure Petrol, and eſſential oils frequently diſtilled, and the ſpiritus rector of plants.

Much more remains to be ſaid of the different ſtates of phlogiſton from its moſt rarefied known ſtate, *viz.* that of inflammable air, to its moſt condenſed ſtate, that in which it is combined with metallic earths, &c. I have already diſtinguiſhed eight intermediate ſtates each differing from the other by the portion of elementary fire they contain, this quantity being, as far I can judge directly, as the rarefaction of the phlogiſton; but theſe reſearches are foreign to my preſent ſubject. I ſhall only remark, that phlogiſton, in a ſtate perhaps 100 times rarer than inflammable air, and conſequently containing much more fire, may poſſibly conſtitute the electric fluid.

P. S. Since I wrote the above, I have been honoured with a letter from Dr. PRIESTLEY, in which he informs me, that he has reduced the calces of iron, copper, lead, and tin, merely by melting them in inflammable air by means of a burning glaſs. A certain quantity of inflammable air was abſorbed by each during their reduction; but the unabſorbed part was equally inflammable, ſo that there was no decompoſition; but the remainder was of the ſame nature as the part abſorbed. He alſo, by the ſame means, converted nitrous vapour into nitrous air, and the phoſphoric acid into phoſphorus. And ſince the communication of the laſt mentioned experiments, which ſeem to him alſo a direct proof of the identity of inflammable air and phlogiſton, he has been ſo obliging as to inform me, that he has revived the calces of metals in *alkaline air* as well as

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in *inflammable air*, and also formed a phosphorus; and that he has little doubt but that he shall be able to produce any thing else in which phlogiston is supposed to be concerned. This, he says, agrees with several of his former experiments, especially that in which he produces inflammable air from alkaline air, by means of the electric spark and volatile alkali from iron, supersaturated with phlogiston by means of nitrous air, which he has repeatedly done since the publication of his last volume. This observation, he adds, may help to explain some things in the theory of chemistry, especially the affinity which all acids have both with *phlogiston* and with *alkalies*; but, he says, that alkaline air contains something else besides phlogiston; because when this air is used, there is always a residuum of something that is *neither alkaline nor inflammable air*; but he wants more sunshine to complete and extend his experiments on this subject *.

OF THE QUANTITY OF PHLOGISTON IN NITROUS AIR.

100 gr. of filings of iron being dissolved in a sufficient quantity of very dilute vitriolic acid produced, with the assistance of heat gradually applied, 155 cubic inches of inflammable air, the barometer at 29,5, and the thermometer between 50 and 60°. Now inflammable air and phlogiston being the same thing, this quantity of inflammable air amounts to 5,42 gr. of phlogiston.

Again, 100 gr. of iron, dissolved in dephlogisticated nitrous acid, in a heat gradually applied and raised to the utmost, afford 83,87 cubic inches of nitrous air. And as this nitrous air con-

* Since this paper was committed to the press, I find that Mr. PELLETIER has reduced the arsenical acid to a regulus, by merely passing inflammable air through the solution of that acid in twice its weight of water. ROZ. Journ. February 1782.

tains nearly the whole quantity of phlogiston which iron will part with (it being more completely dephlogisticated by this acid than by any other means) it follows, that 83,87 cubic inches of nitrous air contain at least 5,42 gr. of phlogiston; but it may reasonably be thought that the whole quantity of phlogiston which iron will part with is not expelled by the vitriolic acid, and that nitrous acid may expel and take up more of it. To try whether this was really so, I calcined a certain quantity of green vitriol, until its ferruginous basis was quite insipid; I then extracted from 64 gr. of this ochre two cubic inches of nitrous air, consequently 100 gr. of this ochre would give 3,12 cubic inches of nitrous air; and if 83,87 cubic inches of nitrous air contain 5,42 of phlogiston, then 3,12 cubic inches of this air contain 0,2 of a grain of phlogiston; consequently, nitrous acid extracts from 100 gr. of iron two tenths of a grain more phlogiston than the vitriolic acid does; therefore 83,87 cubic inches of nitrous air, containing nearly all the phlogiston which iron gives out, contain 5,62 gr. of phlogiston.

Then 100 *cubic inches of nitrous air contain* 6,7 *gr. of phlogiston*, and since 100 cubic inches of nitrous air weigh 39,9 gr. they must also contain 33,2 *gr. of nitrous acid.*

Also, 100 *gr. of nitrous air contain* 16,792 *of phlogiston, and* 83,208 *of acid.*

When first I made these experiments I imagined, that the nitrous air thus expelled contained all the phlogiston of the metals dissolved in the nitrous acid, as this acid is well known to dephlogisticate metals as perfectly as possible; but I soon observed, as did Dr. PRIESTLEY and Mr. FONTANA, that the greater part of this is air resorbed and detained in the solution, the acid and calx having, according to the beautiful remark of Mr. SCHEELE, a greater attraction to phlogiston than either separately; yet that the calculation

calculation is nearly juſt, will appear clearly in my next paper, by its coincidence with the quantity of phlogiſton diſcovered in lead by Dr. PRIESTLEY and that which is contained very evidently in regulus of arſenic, ſilver, and quickſilver.

OF THE QUANTITY OF PHLOGISTON IN FIXED AIR.

Before I attempt to determine this quantity, it will be neceſſary to prove that it contains any; and for this purpoſe minutely to examine its nature and origin.

Dr. PRIESTLEY firſt diſcovered that in all proceſſes, wherein phlogiſton is diſengaged from any ſubſtance, as in *combuſtion, reſpiration, calcination of metals, putrefaction, decompoſition of nitrous air by reſpirable air*, &c. fixed air is precipitated from the common or dephlogiſticated air in which theſe proceſſes are performed, and that theſe laſt airs are diminiſhed both in weight and bulk, and are afterwards leſs fit, or abſolutely unfit, for theſe proceſſes, according to the quantity of phlogiſton that was ſet looſe. Theſe facts are admitted by all, let their ſyſtems be what they may. However, Dr. PRIESTLEY thinks he has ſeen one exception to this general rule; for, he ſays, that in the combuſtion of inflammable and common air no fixed air is precipitated, 5 PR. 124. He alſo ſeems inclined to admit another exception in the caſe of the combuſtion of ſulphur.

The queſtions that here ariſe are, firſt, whether the fixed air that appears in theſe circumſtances proceeded from the reſpirable air or not? Secondly, If it proceeded from the reſpirable air, whether it pre-exiſted in that air; or whether it was generated

generated during the proceſs that exhibits it? and if ſo, what are its conſtituent parts?

The firſt queſtion is eaſily anſwered; for in ſuch phlogiſtic proceſſes as are attended with the deſtruction of the ſubſtances that are known to contain fixed air, as thoſe of the animal and vegetable kingdom, the fixed air may be ſuppoſed to proceed in many caſes, both from the decompoſed ſubſtance and from the reſpirable air; and of this ſort are the proceſſes of combuſtion of moſt animal and vegetable ſubſtances, and fermentation; but the fixed air, that appears in ſuch phlogiſtic proceſſes as are performed on ſubſtances that contain no fixed air, muſt be deemed to proceed from the reſpirable air ſingly. And of this caſe we have four clear inſtances; the calcination of metals; the decompoſition of nitrous air by reſpirable air; the diminution of common air by the electric ſpark; and, laſtly, its diminution by amalgamation.

And firſt as to the calcination of metals, Dr. PRIESTLEY has obſerved, that by this operation reſpirable air (and only reſpirable air) is diminiſhed between one-fourth and one-fifth, both in its weight and bulk; but Mr. LAVOISIER has demonſtrated, that nothing is loſt or eſcapes through the veſſels (as Mr. SCHEELE would have it); for the weight and materials continue undiminiſhed when the operation is performed in cloſe veſſels*. That part, therefore, which the air loſes is taken up by the metallic calx, which accordingly is found to gain the very weight which the air loſes. Now the air contained in the calx is fixed air; for Mr. LAVOISIER alſo obſerved, that by the calcination of lead, by ſolar heat, over lime-water, the water was rendered ſlightly turbid†. It is true, that

* Mem. Par. 1774.

† I LAVOIS. 291.

that Dr. PRIESTLEY, in a similar experiment, did not observe this turbidity; but he accounts for this circumstance very justly, by supposing, that the calx of lead absorbed the fixed air preferably to the lime. And this supposition is not gratuitous; for metallic calces, and particularly those of lead, are known to attract fixed air as strongly as quick lime, or rather more strongly *: and what sets this matter beyond all doubt, the calces of lead all yield fixed air by heat, and the grey calx of lead, in particular, which was that produced by Dr. PRIESTLEY, in the experiment to which I allude, affords by heat fixed air only. Other calces of lead after fixed air afford also dephlogisticated air; but this I shall shew also to have been originally fixed air. If filings of iron be mixed with water in close vessels, they will be converted into rust, and the incumbent air diminished one-fourth, as Mr. LAVOISIER attests †; but Dr. PRIESTLEY has shewn, that rust of iron yields scarce any other than fixed air, which may be expelled out of it by mere heat ‡. Nay, iron alone, exposed to common air over a vessel of water for three months, reduced this air one-fifth; and being exposed to dephlogisticated air, over a vessel of mercury, it reduced it one-tenth in nine months §. In all these cases the fixed air could surely come from nothing else but the incumbent respirable air and the phlogiston of the metal.

Secondly, It is well known, that if nitrous air be decomposed by respirable air over lime-water, the lime will be precipitated ‖. In this case also, the fixed air must proceed from the

* VOGEL, § 599. 2 N. Act. Upsal. 240. IX Mem. Scav. Etrang. 544.

† 1 LAVOIS. 192.

‡ 2 PR. 112.

§ 2 PR. 182. 4 PR. 253.

‖ 1 PR. 114. 3 PR. 30. 1 PR. 138.

respirable

reſpirable air and the phlogiſton of the nitrous air; for it cannot proceed from the nitrous acid, as this acid is not decompoſed, but is taken up by the water over which the mixture of both airs is made, as Mr. BEWLY has undeniably proved: and hence it is, that unleſs a large quantity of lime-water be uſed ſo as to contain enough for both the nitrous and aërial acids to act on, there will be no precipitation of lime, as Mr. FONTANA has obſerved; for the nitrous acid will ſeize on the lime preferably to the aërial. Dr. PRIESTLEY indeed obſerved, that if a bladder, filled with nitrous air, be dipped in lime-water, it occaſions a precipitation of lime on the ſurface of the water. 1 PR. 213. But he elſewhere acknowledges, that this proceeds from the inability of the bladder to confine nitrous air. 1 PR. 76. and 128, which Mr. BAUME alſo long ago obſerved, without knowing any thing more of this air. BAUME *ſur l'Æther*, 285. The phlogiſton paſſes through the bladder, and unites to the common air contiguous to it*. Beſides, nitrous air acts on the bladder itſelf, and extracts fixed air from it. 1 PR. 214. Hence alſo, if rain-water carefully boiled, and freed from its own air, be made to abſorb a quantity of nitrous air, it will again, on boiling, yield it back as pure as at firſt; but if common water be made to imbibe nitrous air in the ſame manner, it will, on boiling, yield alſo a portion of fixed air. 3 PR. 109. Does not this happen clearly becauſe common water contains atmoſpheric air, or air ſomewhat purer, which is converted into fixed air by mixture with the nitrous air? This experiment alſo ſhews, that water itſelf never unites to phlogiſton, ſince it does not take any from nitrous air, where the union of phlogiſton to the acid is of the laxeſt kind.

* 3 PR. 156.

6 Thirdly,

Thirdly, If the electric spark be taken through common air, this air will be diminished one-fourth, and a solution of lime, if contiguous, will be precipitated, and a solution of turnsole tinged red. I PR. 184. 186. Whence could the fixed air here produced proceed, but from the common air, and the phlogiston of the metallic conductors? This excellent philosopher has even shewn it could proceed from nothing else; for after that air had contributed all it could to that production, that is, was diminished to the utmost, he changed the liquors, but could produce no change in their colour, nor the least sign of fixed air. This experiment has also been repeated in France, and the inside of the glass tube, in which the common air was contained, was moistened with a solution of caustic fixed alkali, and the alkali, after the operation, was found crystallized; but when the tube was exhausted of air, and the experiment repeated, no change whatsoever was found in the alkali. *Essai sur l'Electricité, par Mr. Le Comte* DE LA CEPEDE, vol. I. p. 155.

Fourthly, If lead and mercury be agitated in a phial, partly filled with common air, this air will be diminished one-fourth, and the residuum will be found completely phlogisticated. The diminution will be still greater if the phial contain dephlogisticated air. I PR. 149. The lead is converted into a calx, calcination being the known effect of the amalgamation of the base metals; and this calx absorbed the fixed air produced, for Dr. PRIESTLEY expelled this air from it. I PR. 144.; and hence an amalgama of lead and mercury decrepitates when heated *. Whence could this fixed air proceed, but from the respirable air? For surely neither lead nor mercury contain any.

* I MALOUIN. 105.

 If

If the above experiments be attended to, the anſwer to the ſecond queſtion will be equally obvious. It is certain, that common air does not conſiſt of one-fourth of its bulk of fixed air; for if it did, the remaining three-fourths muſt be dephlogiſticated air: and if ſo, then the abſolute weight of a mixture of three-fourths dephlogiſticated air and one-fourth fixed air ſhould coincide at leaſt nearly with the abſolute weight of an equal bulk of common air; but in fact it is very far from it: for four cubic inches of common air weighed 1,54 gr.; but a mixture of three cubic inches of dephlogiſticated air and one of fixed air weighs 1,83 gr.; neither indeed has ſo large a portion of fixed air been ever ſuppoſed to exiſt in common air. Beſides, if fixed air pre-exiſted in common air, it might be ſeparated from it by lime-water, at leaſt in ſome degree. I have mixed one part of fixed air with twenty of dephlogiſticated air, and alſo with twenty of phlogiſticated air in cloſe veſſels, and theſe mixtures did not fail to render lime-water turbid. But let common air be agitated in lime-water ever ſo long in cloſe veſſels, not the leaſt cloudineſs will appear; nor does quick-lime, in theſe circumſtances, in the leaſt affect common air, as Dr. PRIESTLEY has obſerved. 2 PR. 184. The ſpontaneous precipitation of lime-water ariſes therefore from an accidental diffuſion of fixed air through common air, and the ſlowneſs of this precipitation ſhews its quantity to be very ſmall. The inference from the above experiments will be much ſtronger againſt the pre-exiſtence of fixed air in reſpirable air, if, inſtead of common air, dephlogiſticated air be uſed; for there the diminution is ſo great, and the quantity of fixed air produced ſo conſiderable, that it can by no means be ſuppoſed to have pre-exiſted, its properties being ſo very oppoſite to thoſe of dephlogiſticated air.

To

To this it has been answered, first, that fixed air in common air is united to some unknown basis, which attracts it more strongly than quick-lime does; but that it is precipitated from that basis by the phlogiston set loose in phlogistic processes, which is still more strongly attracted by that basis; and, secondly, that the diminution both of the weight and bulk of respirable air in phlogistic processes does not arise intirely from the separation of fixed air, but from some other cause.

But neither of these answers is satisfactory: for the supposition of such a basis is evidently gratuitous, being supported by not one experiment. It is also contrary to analogy, there being no instance of the separation of fixed air, nor of any other acid, from any substance merely by the greater affinity of phlogiston to such substance. It is also insufficient for the purpose for which it was framed; for of dephlogisticated air 97 parts in 100 are reducible to fixed air by phlogistic processes; and can it be imagined, that 97 parts in 100 of it were mere fixed air united to less than three parts of an unknown basis? I say, less than three parts; for, according to the present supposition, this unknown basis took up the phlogiston of the substance that separated the fixed air from it, and yet it, and the whole quantity of phlogiston it took up, amounted but to three parts of an hundred; can it be supposed, that this vast proportion of fixed air would not in the least affect lime-water, as pure dephlogisticated air is known not to do? Can it be supposed, that such an immense quantity of fixed air, combined with any basis, would be so superlatively fitted for all phlogistic processes, while fixed air, in its disengaged state, is totally unfit for them? Besides, this unknown basis, after all, is nothing but phlogisticated air, with which fixed air is incapable of contracting any union; and if its phlogiston be washed away, it is not

 found

found different from common air ſlightly injured. Accordingly, we find that this conjecture, firſt advanced by Dr. PRIESTLEY in the infancy of his reſearches, is now abandoned by him. Vol. V. p. 31. And he now juſtly thinks, that common air does not contain above $\frac{1}{52}$ of its bulk of fixed air.

As to the diminution of bulk, it is certain, that the whole of it does not proceed from the ſeparation of fixed air; for though no part of the fixed air ſhould be abſorbed, yet ſince part of the common air is converted into fixed air, there muſt be a diminution of bulk, ſince fixed air is ſpecifically heavier than common air, and the bulks are inverſely as the ſpecific gravities; but the diminution of *maſs* muſt wholly, and that of bulk muſt alſo for the greater part ariſe from the abſorption of fixed air by water, or the ſubſtance from which the phlogiſton proceeds. I have ſucceſſively added ſix meaſures of nitrous air to two of dephlogiſticated air from precipitate *per ſe*, and after each addition transferred the mixture into freſh lime-water, and after each I found the lime precipitated until the whole was reduced to one-tenth nearly, ſo that nine-tenths of this dephlogiſticated air was evidently converted into fixed air; and ſince fixed air did not pre-exiſt in the dephlogiſticated air, it was evidently produced by the union of the phlogiſton of the nitrous air with the truly dephlogiſticated part of the dephlogiſticated air.

Here we ſee how fixed air is generated in moſt other phlogiſtic proceſſes, performed in common air. The phlogiſton is attracted by the dephlogiſticated part of common air, unites to it, expels part of its fire, and ſo forms fixed air; yet a part of this pure air generally eſcapes the action of phlogiſton, being protected from it by the quantity of phlogiſticated air which is always found in common air, and which forms about two-thirds of it, in the ſame manner as gold is protected by

ſilver,

silver, and silver by gold, from the action of their respective menstruums; and this is the reason why, in some phlogistic processes, the diminution is greater than in others; and why the diminution continues to increase slowly for a long time.

Nor is the supposition, that common air consists of two fluids, one phlogisticated and the other dephlogisticated, gratuitous; it is pointed out by several experiments. If a mixture be made of three parts phlogisticated air and one of dephlogisticated air, it will exactly perform the functions of common air; a candle will burn in it, an animal will live in it, just as in common air *. Besides, common air may in some measure be separated into these constituent parts by lying over pure water; for dephlogisticated air is much more miscible with water than common air, as Mr. FONTANA remarked, Phil Transf. 1779, p. 443. and 444 †, and SCHEELE on Fire, § 94. Hence, if common air be suffered to stand some time over pure water, it will be diminished, the purer part being in great measure absorbed by the water, and the remainder will be found to consist of so large a proportion of phlogisticated air that a candle will not burn in it. 1 PR. 158. 4 PR. 353. Mr. SCHEELE again expelled that part which the water had absorbed, and found it dephlogisticated. He also found, that phlogisticated air is not at all absorbed by water. ibid.

Hence we see, why the whole of any quantity of common air can never be converted into fixed air; for no part of it will unite with phlogiston, but the dephlogisticated part (which never exceeds one-third of the whole). This Mr. SCHEELE has decisively proved by exposing liver of sulphur to a mixture

* Mem. Par. 1777, p. 191.

† He informed me, that water takes up one-fourteenth of its bulk of dephlogisticated air, and only one-twenty-eighth of common air.

of

of phlogiſticated and dephlogiſticated air; the mixture was diminiſhed in the ſame proportion as it contained dephlogiſticated air, and no more. SCHEELE, § 43.

Phlogiſticated air, therefore, is not the uſual product of common phlogiſtic proceſſes; but the phlogiſticated reſiduum that is found after ſuch proceſſes muſt have pre-exiſted, as that evidently does which is found after the mixture of nitrous and very pure dephlogiſticated air, for almoſt the whole of this laſt is turned into air which is abſorbed by water, and precipitates lime, as we have already ſeen, ſo that no part of it is converted into phlogiſticated air, this being immiſcible with water. Now common air is affected by nitrous air juſt in the ſame manner, and differs only in degree; therefore the phlogiſticated air, which is found after its phlogiſtication in the uſual proceſſes, was not produced by thoſe operations, but pre-exiſted.

Phlogiſticated air conſiſts of fixed air ſuper-ſaturated with phlogiſton, as ſulphur does of volatile vitriolic acid ſuper-ſaturated with phlogiſton; and as ſulphur is not generally formed when the vitriolic acid unites to phlogiſton, but only volatile vitriolic acid, ſo neither is phlogiſticated air each time that pure air unites to phlogiſton, but rather fixed air. I ſay *ſuper-ſaturated*, becauſe it contains ſuch a quantity of phlogiſton as to be inſoluble in water. Many experiments of Dr. PRIESTLEY clearly point out this compoſition. Thus that celebrated philoſopher has found, that if phlogiſticated air be agitated in water, out of which its air had been boiled, and whoſe ſurface is expoſed to the atmoſphere, it will be in great meaſure purified (juſt as ſulphur is decompoſed by trituration in water), and if then it be paſſed through lime-water two or three times, it renders it turbid. 2 PR. 218. Here then the exceſs of phlogiſton, by reaſon of its repulſion from water, is eaſily

eaſily attracted by the dephlogiſticated part of the common atmoſphere, which is immediately imbibed by the water out of which its air had been boiled; the phlogiſticated air is thereby decompoſed and partly turned into fixed air, which makes the lime-water turbid. Part alſo of the fixed air is decompoſed as will preſently be ſeen, and hence the degree of purity which it acquires. Further, if the electric ſpark be taken in fixed air, three-fourths of it will be rendered inſoluble in water, and the whole will probably become ſo if the operation be long enough continued. 1 PR. 248. This inſoluble reſiduum Mr. FONTANA found to be phlogiſticated air; and that, if this phlogiſticated air be agitated in water (whoſe ſurface is expoſed to the atmoſphere) it will become again common air. *Recherches Phyſiques*, 77. That is, it will acquire a degree of purity nearly the ſame as that of common air. This fully confirms all that has been hitherto ſaid concerning theſe airs; ſo alſo, if a mixture of filings of iron and ſulphur, made into a paſte, be expoſed to fixed air, and made to ferment, part of the fixed air will be turned into phlogiſticated air, 3 PR. 257. Juſt as in another equally curious experiment he found, that vitriolic air was converted into ſulphur by the gradual exhalation of phlogiſton from a ſolution of that air in water, and as it daily happens in the hot baths at Aix la Chapelle. And hence we ſee, that fixed air, even in its elaſtic ſtate, is capable of taking an exceſs of phlogiſton, when this laſt is inſenſibly ſeparated from any ſubſtance, and then becomes phlogiſticated air. Phlogiſticated air may alſo be formed by a rapid and copious affluence of phlogiſton, in certain circumſtances, as we ſhall ſoon ſee. I ſhould not omit, that phlogiſticated air, after it has been purified from phlogiſton by agitation in water, is again diminiſhable by phlogiſtic proceſſes, and that fixed air is preci-

pitated from it as usual. 2 PR. 219. A circumstance which at that time was thought inexplicable, and which indeed is so, on any other principles but those here laid down, of which it is an immediate consequence.

Having thus far synthetically proved the constituent parts of fixed air to be pure elementary air and phlogiston, I shall now endeavour to do the same by its analysis: and, in the first place, that it contains phlogiston, and even in such quantity as to deserve to be classed among the phlogisticated acids, appears by its action on *black manganese*. This semi-metallic calx, as has been proved by that admirable chemist Mr. SCHEELE, is completely soluble only in phlogisticated acids, and is precipitable from them by fixed alkalies in the form of a white calx. He also found, that this manganese is also soluble in water strongly impregnated with fixed air, and is also precipitable from it in the form of a *white calx*. 35 Mem. Stock. p. 96.

If fixed air be repeatedly dissolved in, and expelled from water, it leaves each time a residuum which is insoluble in water, diminishable by nitrous air, and capable of supporting animal life. Hence it is evidently decomposed, the phlogiston separating from it, and gradually uniting to the common atmosphere by reason of the repulsive power betwixt it and water. Dr. PRIESTLEY indeed found, that a candle would not burn in it; but this arises only from a mixture of a small quantity of fixed air not yet decomposed, of which, according to the experiments of Mr. CAVENDISH, one-ninth is sufficient to extinguish a candle *.

Again, Mr. ACHARD has converted fixed air into air of nearly the same purity as common air by passing it five or six times through melted nitre. Mem. Berlin. 1778. Mr. CAVALLO

* 1 PR. 34. 40. 2 PR. 219, 220.

6 passed

passed it but once through melted nitre, and yet found it considerably meliorated, for it was diminished by nitrous air. In this case the nitrous acid attracted the phlogiston; for it is known to become phlogisticated by the fusion of nitre, so as to be expellable even by the vegetable acids. 2 N. Act. Upf. 171. And aqua regia may be made by mixing nitre with marine acid.

I shall now briefly consider what may be said in opposition to this doctrine.

In the first place it may be difficult to conceive, that the addition of phlogiston should render any substance more soluble in water, as it is known to render most acids less soluble in that liquid; but a little attention will shew, that phlogiston does not always render substances less soluble in water than they were before; for the acid of sugar is less soluble in water than sugar itself, though sugar consists of that acid united to phlogiston. The dephlogisticated marine acid unites more difficultly with water than the same acid does when phlogisticated, as the illustrious BERGMAN has observed*. Caustic volatile alkali has been decomposed by Mr. SCHEELE, and found to consist of an air insoluble in water, and phlogiston; so that it is rendered soluble in water only by union with phlogiston. It would be foreign to the subject to enter into the reason of these exceptions, but the facts are certain.

Another objection may be drawn from a remarkable experiment to be found in the fifth volume of Dr. PRIESTLEY's observations, where it is said, that inflammable air and common air being fired by an electric spark over lime-water, the diminution took place all once, and the lime was not precipitated; but as it is equally true, that fixed air is precipitated by other phlogistic processes, this experiment proves only, that in these

* Anleitung, § 333.

particular circumſtances, where a large quantity of phlogiſton is ſuddenly heated and transferred all at once upon the dephlogiſticated part of common air, phlogiſticated air may be formed as ſulphur and volatile acid is formed, when a large quantity of hot phlogiſton is united all at once to the vitriolic acid.

Analogous to this is another experiment of Mr. CAVALLO's, where he found, that, by the exploſion of gunpowder, a large quantity of phlogiſticated air is produced *; and alſo another of Dr. PRIESTLEY's, wherein he found, that by firing a mixture of equal parts, ſulphur and nitre, only one-twelfth of the air produced was fixed air, the remainder being phlogiſticated air. But I own the circumſtances of the former experiment are not as yet well known to me, not having been able to repeat it in ſuch a manner as to remove all doubt either of the eſcape of the air through the cement which fixes the wire that conducts the electric fire, during combuſtion; or that the ſmall quantity of inflammable air uſed prevents the fixed from being ſenſible. It may alſo happen, that to the production of fixed air it is neceſſary that the phlogiſton be condenſed to a certain degree, as it is in common caſes; and perhaps, when exceedingly rarified, as it is in inflammable air from metals, it forms ſome other, as yet unknown, compound. Thus much is certain, that all other inflammable air, fired with the electric ſpark, produces fixed air; and all other inflammable air is ſpecifically heavier than the metallic, and before inflammation evidently contains no fixed air. Mr. WARLTIRE, after burning metallic inflammable air, found a *white powdery ſubſtance* (probably a calx) which may have abſorbed the fixed air.

However, in the common proceſs of combuſtion of animal and vegetable ſubſtances it is certain, that fixed air is ſeparated

* CAVALLO on Air, p. 812.

from

from common air, and that the whole diminution is owing to its production and absorbtion. Mr. LAVOISIER has set these points in the clearest light. He introduced a lighted candle into a receiver standing on mercury: the air at first expanded by reason of the heat, and the candle was shortly after extinguished; but when all was cold, there was scarcely any diminution. He then introduced, under the receiver, a caustic fixed alkaline liquor: the air was immediately diminished, and the diminution reached nearly one-ninth of the whole. He then introduced a small quantity of vitriolic acid; the alkali immediately effervesced, gave out its fixed air, the mercury redescended, and the air in the receiver occupied the same space as at first; so that this experiment is perfectly conclusive. He also lighted a candle in dephlogisticated air, and when it was extinguished, introduced a caustic fixed alkaline liquor, and then, and only then, this air was diminished two-thirds, by which it is evident, that two-thirds of it were converted into fixed air; but the remaining third was so far from being phlogisticated air, that a candle burned in it as well as ever, and after it went out half of this air was absorbed by a caustic fixed alkali, and the remainder was still little worse than common air. Mem. Par. 1777, p. 195, &c.

Yet Mr. LAVOISIER thinks, that by the calcination of metals fixed air is not produced; but that the metals absorb the dephlogisticated part of common air, and are thereby converted into a calx. And on this is founded his extraordinary opinion of the non-existence of phlogiston; whereas it is evident, that even mercury affords inflammable air, and consequently contains phlogiston, and that it loses part of this during calcination, and consequently fixed air must be produced, as he himself acknowledges it to be during combustion, by the union of inflam-

mable air and the dephlogiſticated part of common air, which after this union is abſorbed by the calx. It is true, that the mercurial calx, and alſo the calces of lead, and many others, yield dephlogiſticated air; but then the mercury is always revived, ſo that it is evident, it retakes the phlogiſton from the fixed air, of which nothing then remains but the dephlogiſticated part, which accordingly appears in the form of dephlogiſticated air. Dr. PRIESTLEY never found the whole of the mercury revived, and accordingly he recovers a little fixed air from the mercurial calx. 2 PR. 217. But Mr. LAVOISIER finds the whole of the mercury revived, and for that reaſon finds no fixed but all dephlogiſticated air; thus their different reſults are clearly explained, and probably proceed from the different degrees of heat they employed, and the different phlogiſtication of their acids. The dephlogiſticated air that is extracted from *minium* proceeds alſo from a partial revivification of the lead, which always takes place*: nor is it wonderful, that this calx ſhould dephlogiſticate fixed air, ſince it dephlogiſticates the marine acid alſo, as Mr. SCHEELE has obſerved †.

To this it will probably be objected, that dephlogiſticated air muſt pre-exiſt in the *minium*, ſince it is expelled by the marine acid; but this does not follow; for if mangancſe be diſſolved in the common marine acid which is phlogiſticated, and afterwards expelled from it by the vitriolic, it will alſo be found dephlogiſticated.

I ſhall now proceed to inveſtigate the proportion of phlogiſton and elementary or reſpirable air in fixed air.

Dr. PRIESTLEY, in the fourth volume of his Obſervations, p. 380. has ſatisfactorily proved, that nitrous air *parts* with as much

* BEAUME, 7. 1 Pott. Lithog. 29. 3 Dict. Chy. 205.

† Kon. Vet. Acad. Handling. vol. XXXV. p. 193.

much phlogiston to common air as an equal bulk of inflammable air does when fired in the same proportion of common air. Now, when inflammable air unites with common air, its whole weight unites to it, as it contains nothing else but pure phlogiston; since, therefore, nitrous air phlogisticates common air to the same degree that inflammable air does, it parts with a quantity of phlogiston equal to the weight of a volume of inflammable air similar to that of nitrous air. Now 100 cubic inches of inflammable air weigh 3,5 gr.; therefore, 100 cubic inches of nitrous air part with 3,5 gr. of phlogiston when they communicate their phlogiston to as much common air as will take it up. I say, that nitrous air *parts* with *as much* phlogiston, because it is certain, that it does not part with the *whole* of its phlogiston to common or dephlogisticated air, for it contains much more, as already shewn, and, as appears by the red colour, it constantly assumes when mixed with common or dephlogisticated air, which colour belongs to the nitrous acid combined with its remaining phlogiston, and not to the fixed air then produced, nor to the phlogisticated air remaining, as is very evident. Hence the acid, thus formed, is volatile. 4 PR. 267.

One measure of the purest dephlogisticated air and two of nitrous air occupy but $\frac{3}{100}$th parts of one measure, as Dr. PRIESTLEY has observed, vol. IV. p. 245. Suppose one measure to contain 100 cubic inches, then the whole very nearly of the nitrous air will disappear, its acid uniting to the water over which the experiment is made, and 97 cubic inches of the dephlogisticated air, which is converted into fixed air by its union with the phlogiston of the nitrous air; therefore 97 cubic inches of dephlogisticated air take up all the phlogiston which 200 cubic inches of nitrous air will part with; and this we

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have found to be ſeven grains; therefore, a weight of fixed air equal to that of 97 cubic inches of dephlogiſticated air and 7 of phlogiſton, will contain 7 gr. of phlogiſton. Now, 97 cubic inches of dephlogiſticated air weigh 40,74 gr.; to which, adding 7 gr. we have the whole weight of the fixed air equal 47,74 gr. = 83,755 cubic inches; and conſequently 100 *cubic inches of fixed air contain* 8,357 *gr. of phlogiſton, and the remainder elementary air.*

100 *gr. of fixed air contain* 14,661 *of phlogiſton and* 85,339 *of elementary air*; which, when ſtripped of phlogiſton, and impregnated with its proper proportion of elementary fire, becomes again dephlogiſticated air. Hence alſo, 100 cubic inches of dephlogiſticated air are converted into fixed air by 7,2165 gr. of phlogiſton, and will be then reduced to the bulk of 86,34 cubic inches.

And reciprocally, 100 cubic inches of fixed air, being decompoſed, will afford 115,821 cubic inches of dephlogiſticated air, and part with 7,2165 gr. of phlogiſton, ſuppoſing the decompoſition to be complete; that is, the dephlogiſticated air abſoutely pure.

Having read the foregoing account of the nature of fixed air to Dr. PRIESTLEY, I had the ſatisfaction to find it met with his entire approbation, which he authorized me to mention, notwithſtanding what he had advanced to the contrary in his laſt publication.

OF THE QUANTITY OF PHLOGISTON IN VITRIOLIC AIR.

The method I purſued was this:

1ſt, I found the quantity of nitrous air a given weight of copper afforded when diſſolved in the dephlogiſticated nitrous acid, and by that means how much phlogiſton it parts with.

2dly, I found the quantity of copper which a given quantity of the dephlogiſticated vitriolic acid could diſſolve; and obſerved, that it could not diſſolve the greateſt quantity of copper without dephlogiſticating a further quantity which it does not diſſolve.

3dly, I found how much it dephlogiſticates what it thoroughly diſſolves, and how much it dephlogiſticates what it barely calcines.

4thly, How much inflammable air a given quantity of copper affords when diſſolved in the vitriolic acid to the greateſt advantage.

5thly, I deduct from the whole quantity of phlogiſton expelled by the vitriolic acid the quantity of it contained in the inflammable air; the remainder ſhews the quantity of it contained in the vitriolic air.

The particulars were as follows:

1ſt, 100 gr. of copper diſſolved in the dephlogiſticated nitrous acid afforded me 67,5 cubic inches of nitrous air, which, according to the before mentioned calculation, contain 4,52 gr. of phlogiſton.

2dly, 100 gr. of real vitriolic acid take up or diſſolve 54,73 of copper, and 100 gr. of copper require about 182,714 gr. of

of real vitriolic acid to diſſolve them. Again, 100 gr. of copper, when diſſolved in the vitriolic acid, retain only as much phlogiſton as is contained in three cubic inches of nitrous air, that is, 0,2 of a grain; therefore, ſince 100 gr. of copper give out 4,52 of phlogiſton, the vitriolic acid ſtrips it of 4,52 − 0,2, that is, 4,32 gr. of phlogiſton.

3dly, To diſſolve 70 gr. of copper in the vitriolic acid, to the greateſt advantage, 20 more muſt be ſlightly dephlogiſticated; therefore, to diſſolve 100 gr. of copper in this acid, 28,6 more muſt be ſlightly dephlogiſticated. 8 grs. of this ſlightly dephlogiſticated calx afforded 4 cubic inches of nitrous air; therefore, 28,6 would afford 14,3, which contain 0,958 gr. of phlogiſton; but 28,6 gr. of copper, before any dephlogiſtication, contain 1,292 gr. of phlogiſton; therefore, they loſe by this ſlight dephlogiſtication 0,344 of a grain of phlogiſton. Hence, when 100 gr. of copper are diſſolved in the vitriolic acid, the quantity of phlogiſton expelled is 4,32 + 0,34 = 4,66 gr.

4thly, The quantity of inflammable air afforded by the moſt advantageous ſolution of 100 gr. of copper in the vitriolic acid is 11 cubic inches, which amount to 0,385 of a grain of phlogiſton

5thly, The ſolution of 100 gr. of copper in the vitriolic acid afforded over mercury 75,71 cubic inches of air; but of this only 11 cubic inches were inflammable air, the remainder therefore was vitriolic acid air, amounting to 64,71 cubic inches.

6thly, Then the whole quantity of phlogiſton expelled during the ſolution of 100 gr. of copper in the vitriolic acid is 4,66 gr.; of this inflammable air contains but 0,385 of a grain: the remainder therefore, which conſiſts of 4,275 gr. muſt be con-

tained in the 64,71 cubic inches of vitriolic air: therefore, 100 *cubic inches of vitriolic air contain* 6,6 *gr. of phlogiston, and* 71,2 *gr. of acid*, and 100 cubic inches of this air weighing 77,8 gr. 100 *gr. of this air contain* 8,48 *gr. of phlogiston and* 91,52 *of acid.*

OF THE QUANTITY OF PHLOGISTON IN SULPHUR.

This I endeavoured to find by estimating the quantity of fixed air produced during its combustion.

To the top of a glass bell, which was open, I firmly tied and cemented a large bladder, destined to receive the air expanded by combustion, a quantity of which generally escapes when this precaution is not used. Under this bell, which contained about 3000 cubic inches of air, I placed a candle of sulphur, weighing 347 gr.; its wick (which was not consumed) weighed half a grain: it was supported by a very thin concave plate of tin, to prevent the sulphur from flowing over during the combustion, and both were supported by an iron wire, fixed on a shelf in a tub of water. As soon as the sulphur was fired with a very feeble flame, it was covered with the bell, the air being squeezed out of the bladder. The inside of the bell was soon filled with white fumes, so that the flame could not be seen. In an hour after, the fumes thoroughly subsided, and all was cold. The water rose within the bell to a height equal to 87,2 cubic inches; whence I deduce that 87,2 cubic inches of fixed air were produced, which contain 7,287 gr. of phlogiston, which separated from the vitriolic acid, and united to the dephlogisticated part of the common air under the bell.

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The candle of ſulphur being weighed, was found to have loſt 20,75 gr.; therefore, 20,75 gr. of ſulphur contain 7,287 gr. of phlogiſton, beſides the quantity of phlogiſton which remained in the vitriolic air. This air muſt have amounted to $20,75 - 7,287 = 13,463$ gr. which contain 1,141 gr. of phlogiſton; therefore, the whole quantity of phlogiſton in 20,75 gr. of ſulphur is 8,428 gr.; therefore, 100 *gr. of ſulphur contain* 40,61 *gr. of phlogiſton and* 59,39 *of vitriolic acid.*

Several attempts have hitherto been made to determine the proportion of the conſtituent parts of ſulphur; but all were evidently defective. The firſt was that of STAHL, who calculated the quantity of phlogiſton from that of the acid remaining after ſlow combuſtion; but as much, both of acid and phlogiſton, was diſſipated, and as the remaining acid was alſo phlogiſticated, and attracted much of the moiſture of the air, no concluſion whatever could be drawn from this experiment. The ſecond method was, to form a liver of ſulphur, and convert this by a gentle long continued heat into a tartar vitriolate, and then calculate the weight a given quantity of alkali would gain by this operation. This was alſo deviſed by STAHL, and followed by BRANDT and NEWMAN, and by it they determined the proportion of phlogiſton to that of acid to be nearly as 1 to 16. But during the formation of the liver of ſulphur, whether in the moiſt or dry way, much of the phlogiſton and acid is diſſipated, as is evident by the vapour and ſmell that proceed from it, their alkali alſo contained fixed air, which it loſt during the operation, and of which they kept no account, as they were ignorant of its exiſtence; and the tartar vitriol formed by them or ſal polycreſte retained much undecompoſed ſulphur, as always happens when it is not ſtrongly heated; ſo that this method alſo was very imperfect, however ſome ſub-

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sequent chemists who made the experiment with more care concluded from it, that sulphur contained one-seventh of phlogiston. EXLEBEN, § 760.

By weighing flowers of sulphur in a perforated brass box in water, I found its specific gravity to be 1,924. It remained in the water a quarter of an hour before any air issued from it, and then some bubbles arose; but when I opened the box, I found the middle part of the flowers quite dry, so that I make no doubt but some air still remained, and that its specific gravity is still greater. Mr. PETIT weighed it in oil, and found its specific gravity 2,344, which I believe to be nearly the truth.

OF THE QUANTITY OF PHLOGISTON IN MARINE ACID AIR.

8 gr. of copper dissolved in colourless spirit of salt afforded but 4,9 cubic inches of air, when the air was received over water, and this air was inflammable.

8,5 gr. of copper being dissolved in the same quantity of the same spirit of salt, and the air received over mercury, afforded 91,28 cubic inches of air; but of these only 4,9 cubic inches were inflammable air; the remainder, therefore, *viz.* 86,38 were marine air, which weigh 56,49 gr.

Now, as spirit of salt certainly does not dephlogisticate copper more than the vitriolic acid does, it follows, that these 4,9 cubic inches of inflammable air, and 86,38 cubic inches of marine air, do not contain more phlogiston than would be separated from the same quantity of copper by the vitriolic acid: and since 100 grains of copper would yield to the vitriolic

acid 4,32 gr. of phlogiſton, 8,5 gr. of copper would yield 0,367 of a grain of phlogiſton; this then is the whole quantity extracted by the marine acid, and contained in 91,28 cubic inches of air, and deducting from this the quantity of phlogiſton contained in 4,9 cubic inches of inflammable air (= 0,171 of a grain), the remainder, *viz.* 0,367 − 0,171 = 0,196 is all the phlogiſton that can be found in 86,38 cubic inches of marine air. Then 100 *cubic inches of marine air can contain but* 0,227 *nearly of a grain of phlogiſton* 65,173 *of acid.*

Hence we ſee why it acts ſo feebly on oils, ſpirit of wine, &c. having a very ſmall affinity to phlogiſton; and why it is not diſlodged from any baſis by uniting with phlogiſton, as the vitriolic and nitrous acids are, its affinity to it being inconſiderable.

AMENDMENT to P. 191. L. 12.

I have lately repeated this experiment, and found that one meafure of alkaline air is faturated by lefs than half of one meafure of fixed air, but more than one-third, conformably to Dr. PRIESTLEY's firft experiment, p. 293.; by which it appears, that 100 gr. of alkaline air require about 120 of fixed air to faturate them: and hence 100 gr. of concrete volatile alkali contain about 53 of fixed air, 44 of mere volatile alkali, and 3 of water.